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EFFECT OF COLEMANITE ADDITIONS ON SINTERING, PROPERTIES, AND MICROSTRUCTURE OF SPODUMENE HEATPROOF CERAMIC

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The effect of colemanite additives on sintering and the properties and microstructure of spodumene ceramic is studied. It is found that to identify the sintering and formation processes of a higher-density structure of ceramic it is most effective to introduce colemanite in the amounts 5 – 7%. Spodumene ceramic with CLTE $(9.8 – 12.9) \times 10^{-7}$ K^{-1}, heat-tolerance greater than 100 heat cycles (800 °C – water), water absorption 0.7 – 5.0%, and mechanical strength under bending 33 – 44 MPa, which all obtain at the sintering temperature 1200°C, was obtained.

Key words: colemanite, spodumene ceramic, sintering, heat-tolerance.

At the present time heatproof ceramic materials enjoy high demand on the world market for household objects (coffee makers, sauce pans, roasting pan for stewing, and others), and manufacturing them is promising and profitable. This is mainly because compared with similar products fabricated from aluminum and iron, ceramic articles are competitive because their components are safe and production is environment friendly. Such articles are not produced in the Republic of Belarus and nearby countries and are imported in small quantities from the Netherlands, Brazil, and other countries.

In this connection it is of theoretical and practical interest for the ceramic industry to develop scientifically validated theoretical and technological principles for producing ceramic materials from heatproof ceramic for household application.

Compositions on the phase diagram of the ternary system $Li_2O – Al_2O_3 – SiO_2$ in the crystallization zones of eucryptite, spodumene, and petalite were studied. This system is of great interest for use as a base for producing ceramic with high heat-tolerance because of the small value of the CLTE. However, these materials have a comparatively narrow range of sintering, considerable porosity, and low mechanical strength, which makes it impossible to use them under conditions where heat and mechanical loads are present simultaneously [1].

A spodumene ceramic for fabricating articles by slip casting was synthesized as a result of previous studies [2]. Prosyanovskoe kaolin KN-83 (GOST 21286–82), “Keramik-Vesko” refractory clay (GOST 9169–75), OVS-020-V quartz sand (GOST 7031–75), technical grade GK-2 alumina (GOST 6912–87), and lithium carbonate (TU 95.1951–89) were used as starting materials.

Ceramic materials with optimal compositions (16 and 21) obtained at calcination temperatures 1100 and 1200°C are characterized by, respectively, the following physical–technical properties: CLTE = $(10.0 – 11.5) \times 10^{-7}$ and $(2.6 – 4.1) \times 10^{-7}$ K^{-1}, firing shrinkage in the range 0 – 0.1 and 0.3 – 0.4%, water absorption 20.6 – 26.1 and 14.1 – 22.3%, and mechanical strength under bending 21 – 22 and 22 – 26 MPa.

As one can see from these properties the fireproof ceramic materials developed on the basis of spodumene had high water absorption. For this reason, the problem of activation of the sintering process in this system remains very topical. The goal is to obtain materials with a high-density structure, which will increase the mechanical strength, heat-tolerance, and service life of articles, the latter being especially important because of the increased use of dishwashing machines.

One of the effective methods of influencing the structure and properties of ceramics is to introduce into the composition of the initial mix components that form a liquid phase in the calcination temperature range by melting or interaction with the formation of a eutectic melt. Sintering a ceramic material occurs with the participation of a liquid phase that fills pores in the samples.

The works of many researchers are devoted to increasing the degree of sintering of spodumene ceramic by means of various mineralizers: US Patent No. 5962351, USSR Inventor’s certificate No. 899507, USSR Inventor’s certificate

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No. 977436, USSR Inventor's certificate No. 1301819, and USSR Inventor's certificate No. 409998 [3 – 6]. Such mineralizers include fritted lithium-containing glass, apatite, $BaCO_3$, LiF, BaO, ZnO, P_2O_5, Fe_2O_5, and others.

The results of these works are often contradictory with respect to the effect of the chemical composition of the melt formed and the temperature dependence of its viscosity on the sintering process and the formation of crystalline phases. In addition, as a rule, some thermal and other properties degrade as the synthesis temperature of the spodumene materials decreases. Aside from this, most known additives are toxic compounds which endanger the health of workers who are working with these compounds.

Analysis of the additives used in manufacturing has shown boron compounds to be preferable, because borates melt at lower temperatures and are strong fluxes, lower the viscosity of the glass phase, decrease the CLTE of the glass phase and therefore raise its heat-resistance, and increase the mechanical strength and chemical stability of the materials.

Since harmful substances must not be present in mix compositions for pastes used for heat-tolerant dinnerware with high-quality characteristics, the nontoxic nature of boron compounds is especially important. However, the relatively high cost of natural and synthetic boron containing components limits their quantitative content in the synthesis of ceramic materials.

To intensify sintering of heat-tolerant ceramic, B_2O_3 was introduced as colemanite provided by the Eti MineWorks G. M. (Turkey) and characterized by the following chemical composition, %:[2] 5.66 SiO_2; 36.54 B_2O_3; 0.35 Al_2O_3; 23.49 CaO; 2.61 MgO; 0.30 Na_2O; 0.07 Fe_2O_3; 30.98 other.

Colemanite is a hydrated calcium borate $Ca_2B_6O_{11} \cdot H_2O$, whose crystalline structure contains complex chains of tetrahedra $B(O, OH)_4$ and triangles BO_3, bound into a triangular structure via the ions Ca^{2+} and buffer molecules H_2O. Colemanite crystallizes in the monoclinic system, forming short-columnar or dipyramidal habit of colorless crystals as well as continuous fine-grain masses. The Mohs hardness is 4 – 4.5 and the density is 2440 – 2450 kg/m^3.

The effect of colemanite on sintering and the properties and structure of the heat-tolerant ceramic was investigated with its content ranging from 1.0 to 7.0% with step 1.0%.

The experimental pastes were prepared using a slip technology by combined wet grinding of all components to residue 1 – 2% on a No. 0063K sieve. The moisture content of the slip after grinding was 42 – 45%. To ensure the required pouring characteristics a complex electrolyte was introduced in the amount 0.53 – 0.56% above 100%, including calcinated soda, liquid sodium glass, and carbon-alkali reagent, into the slip. The articles were poured into a gypsum mold by the filling method. The intermediate products were dried under natural conditions to residual moisture content not exceeding 0.5%. The dried articles were calcined in periodic electric furnaces at temperatures 1100 and 1200°C, soaked at the final temperature for 1 h to complete the physical-chemical processes occurring during sintering of pastes. The total calcination time, including cooling, was 10 h.

The degree of sintering of the experimental ceramic samples was evaluated according to the firing shrinkage, water absorption, apparent density, and open porosity.

When colemanite is added, the shrinkage, as a main criterion of compaction, uniformly increases. This attests to a gradual increase of the amount of glass phase and an increase of the degree of sintering of the ceramic. Thus, for firing temperature 1100°C the firing shrinkage of the samples is 0 – 0.1% for materials without an additive and 2.4% – 2.8% for 7% additive, reaching at 1200°C reaches 8.8 – 9.0% with 7% colemanite.

A correlation of the effect of an additive on other properties of the samples is also observed. For firing temperature 1100°C, as the amount of the colemanite introduced into the samples increases, the water absorption and porosity decrease and the density increases smoothly. For ceramic samples containing 5% colemanite the water absorption decreases to 18.4 – 18.9%, and the apparent density increases to 1610 – 1640 kg/m^3. When the colemanite content increases to 7% the water content is observed to decrease further to 11.3 – 18.0%; correspondingly, the apparent density also changes — increasing to 1660 – 1710 kg/m^3.

Structural compaction in materials starts to develop actively only at 1200°C, when the amount of melt increases significantly, the viscosity of the melt decreases, surface tension forces appear, and the penetration into microcapillaries increases. At the same time diffusion processes in the solid phase are activated. The combination of both processes results in compaction of the material, as a result of which water absorption in the samples decreases and the apparent density of the samples increases. The introduction of 5% colemanite makes it possible to decrease water absorption to 4.3 – 5.0% with apparent density increasing to 1770 – 1850 kg/m^3. The lowest values of the water absorption were obtained by introducing 7% colemanite and equal 0.1 – 1.7% with a 1.2-fold increase of the apparent density.

The measurements of the bending strength of a ceramic in the presence of a colemanite addition are presented in Fig. 1. The low values of the strength of the ceramic obtained are due to the presence of porosity in the material and are associated with the method used to form the ceramic paste (slip casting in porous molds), well known not to give an adequate particle packing density.

Samples with no additives had the lowest strength. As the colemanite content in the mix increases, the strength characteristic of the samples of synthesized material increases. The strength of the ceramic also increases as the sintering temperature increases from 1100 to 1200°C on average by 50 – 60%. The highest strength indicators are characteristic for samples with 7% colemanite with sintering temperature 1200°C and equal 41 – 44 MPa.

[2] Here and below — content by weight.

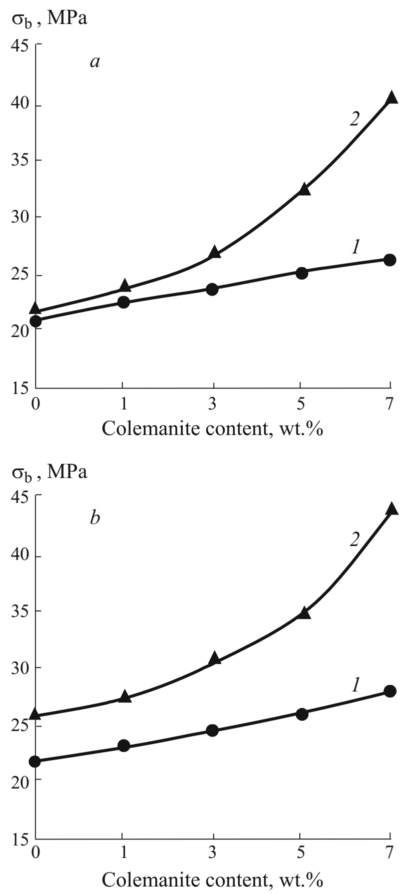

Fig. 1. Bending strength σ_b of samples based on the compositions 16 (*a*) and 21 (*b*) versus the colemanite content: *1*, *2*) firing temperature 1100 and 1200°C, respectively.

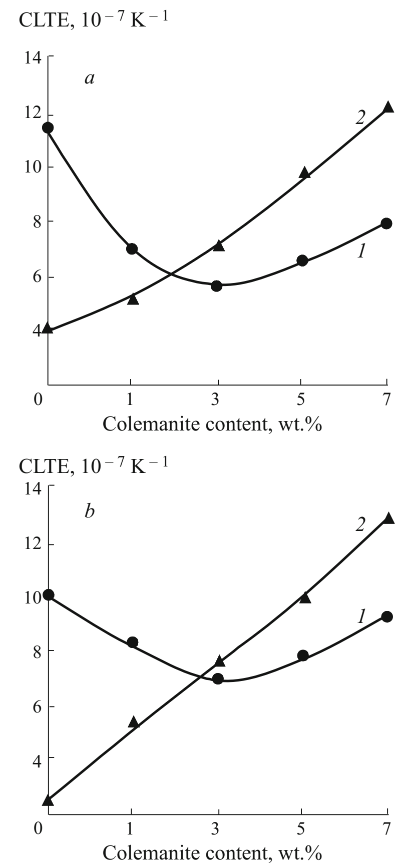

Fig. 2. CLTE of the samples based on the compositions 16 (*a*) and 21 (*b*) versus the colemanite content: *1*, *2*) firing temperature 1100 and 1200°C, respectively.

It is well known that the heat-tolerance of a material is a complex characteristic that depends on many factors. Analysis of heat-tolerance criteria for ceramic shows that properties such as the CLTE, the mechanical strength, and the elastic modulus have the greatest effect on the heat-tolerance; these properties determine the main heat-resistance criterion. The conditions of heat transfer, size and shape of articles, and other factors play a definite role. The character of the structure of a material, on which depend the rate of formation and propagation of thermal cracks, is important [7].

However, the prevailing factor determining the resistance of a ceramic to thermal shock is the CLTE; the lower its indicators, the less likely thermal stresses are to appear in the presence of sharp temperature differentials. The CLTE of a ceramic depends on its phase composition, the form and amount of the cementing glassy phase, and to some extent on the texture and microstructure of the material, which in turn are determined by the degree and character of the sintering [8].

A study of the correlations between the CLTE of the experimental samples versus the amount of additive and the synthesis temperature showed a complicated dependence on the indicated factors (Fig. 2). When colemanite is added the values of the CLTE of the materials change in the range 5.3×10^{-7} to 12.9×10^{-7} K^{-1} depending on the composition.

At firing temperature 1100°C and colemanite content 1 – 3% in the paste the CLTE of the samples decreases as compared with the initial compositions synthesized at the same temperature. In this case part of the glass phase crystallized with formation of an additional amount of β-spodumene.

As the sintering temperature increases to 1200°C, the values of the CLTE of the samples increase as the amount of colemanite added. This is promoted by a decrease of the β-spodumene fraction and by enrichment of the glass phase by calcium cations.

A study of the heat tolerance of synthesized ceramic confirmed its high resistance to thermal shock. The samples were heated to 800°C, soaked in a furnace for 30 min, and then placed in a vessel with flowing water at temperature 10°C. The investigations showed that no changes of color, shape, and size of the samples or cracking occurred; the ceramic samples withstood 100 heating – cooling cycles without fracturing.

The high resistance of lithium-containing minerals to heat shocks is related with the anisotropy of the thermal ex-

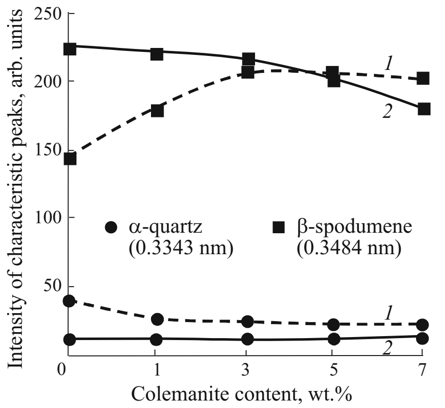

Fig. 3. Relative intensity of the separation of the crystalline phases of the samples based on composition 21 versus the colemanite content: *1* and *2*) firing temperature 1100 and 1200°C, respectively.

pansion, characteristic for compounds possessing a screw axis of symmetry in the direction of which expansion or compression under heating occurs. During heating of crystals which are characterized by anisotropy of the thermal expansion the angles between the directions of the chemical bonds change discontinuously and the interatomic distances in the lattice changes, which is not accompanied by the formation of new symmetry elements in the structure of the material.

It is well known [1] that in β-spodumene the spiral chains consisting of silicon-oxygen and aluminum-oxygen tetrahedra are arranged in the lattice around a four-fold screw axis of symmetry. At room temperature substantial stresses exist in the lattice with such a structure. In the course of heating the arrangement of the tetrahedra $[AlO_4]$ and $[SiO_4]$ changes in a manner where the unit-cell parameter a decreases and c increases. The character of the change of the spiral chains from silicon-oxygen to aluminum-oxygen tetrahedra in the structure of β-spodumene can be compared with the behavior of a spiral spring subjected to deformation.

Figure 3 illustrates the results of x-ray phase analysis of the experimental samples. The study of the phase composition of the materials showed that the samples have a qualitatively similar composition, represented by β-spodumene and its solid solutions with quartz.

The curves of the intensity variations of the x-ray reflections attest that the spodumene component is present in large quantities in the samples; the content of the quartz-containing phase is negligible. As the firing temperature increases to 1200°C the content of the spodumene phase increases appreciably while at the same time the amount of the crystalline quarts decreases; undoubtedly, this affects the thermal expansion of the ceramic, which reaches its lowest value.

When colemanite is added, the intensity of the diffraction peaks of β-spodumene in samples synthesized at 1200°C decreases somewhat as compared with the ceramic having the initial composition.

The differences in the values of the physical-technical characteristics of samples with colemanite addition are related with the structural characteristics of these materials. The microstructure of the samples synthesized at 1200°C, which was studied using a JEOL JSM-5610 LV scanning electron microscope, is shown in Fig. 4.

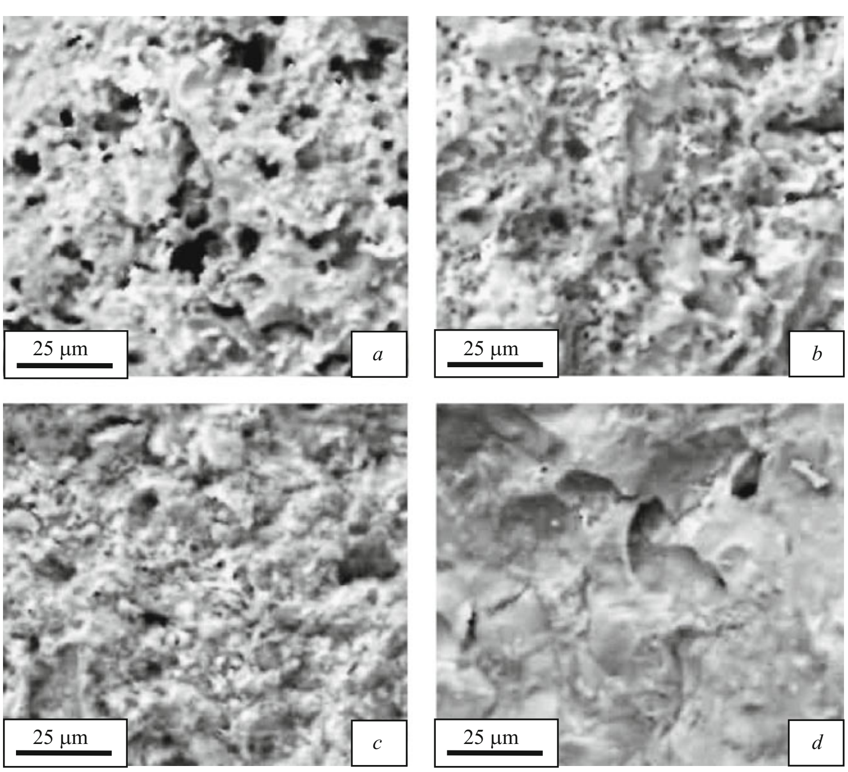

Fig. 4. Electron-microscopic photographs of a section of ceramic samples, based on composition 21, which were fired at 1200°C and have different colemanite content: no colemanite (*a*); 3% (*b*); 5% (*c*); 7% (*d*).

The sample with the initial composition 21 has a uniform structure with developed penetrable, communicating pores reaching 10 – 12 μm in size. It is evident from Fig. 4 that with a constant increase of the amount of colemanite added the structure of the material densifies and the number and size of the pores decreases.

Thus, the microstructure of the samples of ceramic obtained by introducing 7% colemanite is characterized by a substantially higher density, uniformity, negligible intergrain porosity, and close interaction between the liquid phase and the crystals. The melt fills the intergrain voids during intense sintering of a ceramic tile and thereby facilitates an increase of the physical-mechanical properties of the material.

Ultimately, the colemanite addition changes the ratio between the crystalline phase, the glass phase, and pores in the material.

In summary, it was established that introducing 5 – 7% colemanite is the most effective way to intensify sintering and formation of a denser structure of the ceramic.

As a result of this investigation a spodumene ceramic was obtained with CLTE $(9.8 - 12.9) \times 10^{-7}\ K^{-1}$, heat-tolerance more than 100 heat cycles (800°C – water), water absorption 0.7 – 5.0%, and mechanical strength under bending 33 – 44 MPa, which are obtained with firing temperature 1200°C. The complex of physical–chemical properties presented for the synthesized heat-tolerant spodumene ceramic recommends it for the manufacture of household articles which are subjected to sharp temperature differences.

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